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ION EXCHANGE MEMBRANE PRETREATMENT METHOD  
[Ion kokan-maku no maeshori hoho]

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## Claims

1. An ion exchange membrane pretreatment method characterized in that a cationic exchange membrane composed of a polymer that has carboxylic acid groups is immersed in or coated with a hydrophilic organic solvent or an aqueous solution thereof, and the ion exchange membrane is impregnated with 0.1-50 wt% of the aforementioned organic solvent.

2. The method of Claim 1 wherein the hydrophilic organic solvent is an organic solvent with high polarity that has solubility at room temperature in water of 0.1g/100g water or greater.

3. The method of Claim 1 or 2 wherein the hydrophilic organic solvent is selected from an alcohol, a polyhydric alcohol, an aldehyde, a ketone, an ester, an amide or a nitrile.

4. The method of Claims 1-3 wherein the concentration of organic solvent in the aqueous solution is 1-100 wt%.

5. The method of any of Claims 1-4 wherein the hydrophilic organic solvent or aqueous solution thereof has an inorganic salt, and contains 0.01-50 parts by weight to 1 part by weight of the organic solvent.

6. The method of any of Claims 1-4 wherein immersion in or coating with the hydrophilic organic solvent or aqueous solution thereof is performed, and then immersion or coating of the inorganic salt aqueous solution is performed.

7. The method of Claim 6 wherein the concentration of inorganic salt in the aqueous solution is 1-100 wt%.

8. The method of Claim 5, 6 or 7 wherein the inorganic salt is an alkali metal salt, an alkaline earth salt, an amine salt or an ammonium salt of hydrochloric acid, sulfuric acid or iodic acid.

9. The method of any of Claims 1-8 wherein the carboxylic acid group is an alkali metal salt or an ammonium salt.

10. The method of any of Claims 1-9 wherein the polymer that has carboxylic acid groups is composed of a fluorine-containing polymer.

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11. The method of any of Claims 1-10 wherein the ion exchange capacity of the carboxylic acid groups is 0.5-4.0 meq/g dry resin.

12. The method of any of Claims 1-11 wherein the cationic exchange membrane is a polymer film laminated membrane that has two or more types of carboxylic acid groups with different ion exchange capacities.

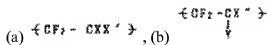
13. The method of any of Claims 1-12 wherein the cationic exchange membrane is a polymer film laminated membrane that has a polymer film having carboxylic acid groups and a polymer film having sulfonic acid groups.

14. The method of Claim 13 wherein the sulfonic acid groups are alkali metal salts or ammonium salts.

15. The method of Claim 13 or 14 wherein the polymer having sulfonic acid [groups] is composed of a fluorine-containing polymer.

16. The method of Claim 13, 14 or 15 wherein the ion exchange capacity of the sulfonic acid groups is 0.3-2.5 meq/g dry resin.

17. The method of any of Claims 9-16 wherein the fluorine-containing polymer is a fluorine-containing polymer having each of the polymer units (a) and (b) below.



Here, X is -F, -Cl, -N or -CF<sub>3</sub>, X' and X" are X or CF<sub>3</sub>(CF<sub>2</sub>)<sub>m</sub>, m is 1-5, and Y is selected from the following.



A method of swelling an ion exchange membrane with a hydrophilic solvent or an aqueous solution thereof beforehand and mounting in an ion exchange membrane electrolytic cell is also known (Japanese Kokai Patent Application No. Sho 52[1977]-72398). It has been reported that limiting of dimensional change when the membrane is used, and improved current efficiency have been achieved with this swelling treatment.

#### Problems to be solved by the invention

However, the prior art as described above has its own problems or shortcomings as below, and is not necessarily favorable.

1. Because application is limited to ion exchange membranes having sulfonic acid groups, it may be unsuited to ion exchange membranes having carboxylic acid groups with different swelling characteristics. (UPS 4,000,057)

2. Although a hydrophilic organic solvent, it is limited to organic amines, which require an operation to form amine groups, a drying process, etc. Industrially, the operation is complicated, and membrane cost will increase, which is undesirable. (Japanese Kokai Patent Application No. Sho 57[1982]-155393)

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3. [The membrane] is immersed in a hydrophilic organic solvent, and the solvent must be removed from the membrane by drying. Industrially, the operation is complicated. (Japanese Kokai Patent Application No. Sho 52[1977]-72398)

#### Means to solve the problems

The present invention was devised to solve the problems described above without sacrificing performance by the ion exchange membrane. The present invention is characterized in that an ion exchange membrane having carboxylic acid groups is immersed in or coated with a hydrophilic organic

solvent or an aqueous solution thereof, and is impregnated with 0.001-1 part by weight of the aforementioned organic solvent, to 1 part by weight of ion exchange membrane.

The present invention improves membrane handling strength and limits the occurrence of creases and dimensional change when the membrane is used by the ion exchange membrane being immersed in or coated with a hydrophilic organic solvent aqueous solution and the ion exchange resin being impregnated with a prescribed quantity of the organic solvent, but this must be performed with the prescribed conditions described below so as not to affect the performance of the ion exchange membrane.

As the hydrophilic organic solvent, an organic solvent with high polarity that has a solubility in water at room temperature (25°C) of 0.1g/100g water or more, and preferably 1g/100g water or more, is preferable. As preferred examples of such an organic solvent, an alcohol, a polyhydric alcohol, an aldehyde, a ketone, an ester, an amide, a nitrile, or mixtures thereof, may be used.

Preferred examples of alcohols include methanol, ethanol, n- or isopropanol, n-iso- or t-butanol, or other hydrocarbon alcohols, preferably with carbon number 4 or less.

Preferred examples of polyhydric alcohols include ethyl glycol, propylene glycol, cellulose and other glycols or derivatives thereof, glycerin, and the like.

Preferred examples of aldehydes include propyl aldehyde and butyl aldehyde. Preferred examples of ketones include acetone and methyl ethyl ketone. A preferred example of amides includes dimethyl formamide. Preferred examples of nitriles include acetonitrile and the like.

When an aqueous solution of a hydrophilic organic solvent is used, the concentration of organic solvent in the aqueous solution is preferably 1-100 wt%, and 5-50 wt% is particularly satisfactory, to impregnate with solvent by appropriate swelling of the membrane.

An inorganic salt can be additionally added to the hydrophilic organic solvent or aqueous solution thereof, and the objective of the present invention can be additionally achieved without lowering the

membrane current efficiency. The quantity added depends on the type of organic solvent and inorganic salt, but is preferably 0.01-50 parts by weight, to 1 part by weight of organic solvent, and 0.1-10 parts by weight in particular may be selected.

The effect produced by adding the aforementioned inorganic salt can also be achieved by immersing the membrane in or coating it with an aqueous solution of the inorganic salt after the membrane is immersed in or coated with the organic solvent or aqueous solution thereof, in lieu of adding the inorganic salt to the organic solvent or aqueous solution thereof. As the aqueous solution of the inorganic salt, it is preferably 1-100 wt%.

Preferred examples of the abovementioned inorganic salts, which are used include alkaline metal, alkali earth metal, amine and ammonium salts of hydrochloric acid, sulfuric acid and iodic acid. Concrete examples of these include sodium chloride, potassium chloride, sodium sulfate, and potassium iodate.

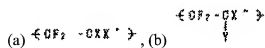
When a hydrophilic organic solvent or an aqueous solution thereof is used, and the ion exchange membrane is immersed in or coated with same, appropriate conditions should be used. For example, in the case of immersion, the conditions used are preferably at 0-90°C, and particularly at 10-40°C, and preferably 1 min to 100 h, and particularly 10 min to 50 h. On the other hand, in the case of coating, the ion exchange membrane is preferably held horizontally, and then the membrane surface is coated from above with the aforementioned organic solvent or aqueous solution. Then, after the membrane is inverted, the organic solvent can be made to penetrate into the film and impregnate it by repeating the aforementioned coating operation again on the opposite side. /4

When either the operation of immersion or coating is applied, the ion exchange membrane should preferably be impregnated with 0.1-50 wt%, and particularly preferably 1-30 wt%, of the hydrophilic organic solvent by the aforementioned operation. If this range is strayed from, the objective of the present invention will absolutely not be achieved, or the effect thereof will be noticeably lower.

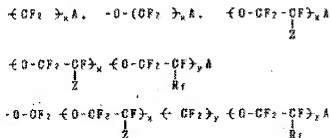


The ion exchange membrane to be pretreated with the present invention is composed of a fluorine-containing polymer preferably having carboxylic acid groups, but the ion exchange membrane used with the present invention is not necessarily formed from only one type of polymer, and does not necessarily have to have only carboxylic acid groups as the ion exchange groups. For example, as the ion exchange membrane, it is possible to use an ion exchange membrane composed of a polymer laminated membrane having two smaller of carboxylic acid groups wherein the anode side is smaller, or a polymer laminated membrane wherein the anode side is weak acid exchange groups, such as carboxylic acid groups, and the cathode side has one or two or more types of strong acid exchange groups such as sulfonic acid groups.

The fluorine-containing polymer having carboxylic acid groups or sulfonic acid groups that constitutes the ion exchange membrane used in the present invention preferably has the polymer units (a) and (b) below.



Here, X is -F, -Cl, -H or -CF<sub>3</sub>, X' is [sic] X" or CF<sub>3</sub>(CF<sub>2</sub>)<sub>m</sub>, m is 1-5, and Y is selected from the following.



x, y and z is each 1-10, Z and R<sub>f</sub> are selected from -F and perfluoroalkyl groups of carbon number 1-10. A represents -SO<sub>3</sub>M, -COOM, water or -SO<sub>2</sub>F, -COF or -COOR, which can be converted to those groups by hydrolysis, M represents an alkali metal or ammonium group, and R represents an alkyl group with carbon number 1-19.

For the cationic exchange membrane that is satisfactorily used in the present invention, the ion exchange capacity of both the carboxylic acid groups and the sulfonic acid groups is preferably 0.5-4.0 milliequivalent/gram of dry resin, and 0.8-2.0 milliequivalent/gram of dry resin is particularly preferable. To provide this ion exchange capacity, with an ion exchange membrane composed of a copolymer that has the aforementioned (a) and (b) polymer units, the (a) polymer units are preferably 1-40 mol%, and 3-25 mol% is particularly appropriate.

The ion exchange membranes are manufactured with a variety of conventional, known methods, and the ion exchange membranes can also be reinforced as necessarily, preferably with a fabric or mesh, or other woven fabric or non-woven fabric composed of a fluorine-containing polymer, such as polytetrafluoroethylene, or a metal mesh, a porous material or the like. The thickness of this invented ion exchange membrane is preferably 50-500  $\mu$ , and could be 100-300  $\mu$  in particular.

In the case of the present invention, a porous layer that contains particles that are gas and liquid permeable and have no electrode activity (Japanese Kokai Patent Applications Nos. Sho 56[1981]-75583 and Sho 57[1982]-39185), or a porous layer that contains particles that are gas and liquid permeable and that have electrode activity (Japanese Kokai Patent Application No. Sho 54[1979]-112398) can be provided as needed on the front surface of the anode of the ion exchange material layer, and membrane resistance can be lowered.

With the present invention, when the ion exchange membrane is treated, the carboxylic acid groups or sulfonic acid groups of the ion exchange membrane are preferably treated in the form of alkali metal salts, alkaline earth metal salts or ammonium salts.

The pretreated ion exchange membrane is then used for a variety of applications, beginning with electrolysis of alkali chloride aqueous solutions, and including electrolysis of water, halogen acids

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(hydrochloric acid, hydrobromic acid), alkali carbonates or other aqueous solutions, electrodialysis of water or aqueous solutions, pervaporation to separate water and alcohol, and the like.

## Operation

In the present invention, although the operating mechanisms for improving handling strength and improving dimensional stability by permeation of the organic solvent is not necessarily clear, it seems that resistance to bending when handled is improved by the organic solvent plasticizing and imparting flexibility to the polymer. It also seems that, for the dimension restricting effect, the organic solvent does not readily volatilize from the membrane and provides a fixed swollen state.

## Effects of the invention

The present invention improves handling strength of the ion exchange membrane, especially resistance to bending, and makes handling easy. Dimensional change when used for electrolysis or the like is also limited, the occurrence of creases is prevented, and problems such as increased cell voltage caused by creasing, and membrane damage, are prevented.

In addition, reduced strength caused by minute scratches in the ion exchange film can be limited.

Note that tensile testing after bending was used as handling strength. This measures reduced strength caused by minute scratches produced by bending stress. An ordinary test piece (No. 1 dumbbell) for tensile strength testing was folded in two with the side covered in cloth on the outside, and after bending 180°C, tensile testing was performed with an ordinary tensile tester, and whether breaks occurred in the bent part was determined. Strength and elongation were measured, and the degree of reduction was determined by comparing with strength and elongation without bending.

### Application Example 1

$\text{CF}_2=\text{CF}_2$  and  $\text{CF}_2=\text{CFO}(\text{CF}_2)_3 \text{COOCH}_3$  were copolymerized, and two types of fluorine-containing polymers with two ion exchange capacities ( $\text{AR}$ ) of 1.25 meq/g and 1.44 meq/g were synthesized. Polytetrafluoroethylene (PTFE), fine powder was kneaded into the fluorine-containing polymer with  $\text{AR}$  1.44 meq/g dry resin, and then a 150  $\mu$  film was obtained by extrusion film formation. This a PTFE woven fabric was put into it using a thermal roll press, a 30  $\mu$  film of the fluorine-containing polymer with  $\text{AR}$  1.25 meq/g was laminated onto the opposite side from the side containing the fabric, and a reinforced laminated membrane was obtained. A  $\text{ZrO}_2$  particle layer was additionally formed on the fabric side, and a  $\text{SiC}$  particle layer on the opposite side.

The membrane was hydrolyzed at 70°C for 18 h in 25%  $\text{NaOH}$ , and carboxylic acid substituents were converted to Na salt type. Next, [the membrane] was immersed in a mixed solution of 80 wt% of 5.2  $\text{NNaCl}$  solution and 20% wt% of ethylene glycol for 20 h at room temperature. When tensile testing was performed after the membrane was bent, no reduction in strength occurred in the bent part. The membrane was placed in an electrolytic cell, the anode solution was held at 35%  $\text{NaOH}$ , and 200 g/L  $\text{NaCl}$  was supplied to the cathode chamber, and when electrolysis occurred under the conditions of 90°C and 30  $\text{A/dm}^2$ , current efficiency was 96%. When the membrane was removed after 300 days of electrolysis, hardly any creasing was seen.

### Comparative Example 1

Other than using 1  $\text{NNaCl}$  solution in lieu of using the ethylene glycol mixed salt solution in Application Example 1, the same was performed. When tensile testing of the membrane after bending was performed, there was breakage in all the bent parts, and it could be seen that the strength in the bent parts

decreased. The break strength in this case was 3.0 kg/cm width, and elongation was 11%. With normal tensile testing, they are 5.4 kg/cm width and 43%, respectively.

#### Application Example 2

Other than using 60 wt% 5.2 NNaCl and 40 wt% glycerin in lieu of the ethylene glycol mixed salt solution in Application Example 1, the same was performed.

The membrane was placed in an electrolytic cell, and when electrolysis was performed the same way as in Application Example 1, current efficiency was 96%, and when the membrane was removed after 300 days of electrolysis, hardly any creasing was seen.

#### Application Example 3

When the same was performed, other than using 1 NNaCl in lieu of using the 5.2 NNaCl solution in Application Example 1, the membrane swelled noticeably. When tensile testing was performed for the membrane, no reduction in strength had occurred at the bent parts. However, when electrolysis was performed with the membrane the same way as in Application Example 1, current efficiency was 92%. /6

#### Application Example 4

When the same was performed, other than using a mixed solution of 60 wt% of 5.2 NNaCl and 40 wt% of methanol, in lieu of using the ethylene glycol mixed solution in Application Example 1, the membrane swelled noticeably. When tensile testing was performed for the membrane, no reduction in strength had occurred at the bent parts. However, when electrolysis was performed with the membrane the same way as in Application Example 1, current efficiency was 90%.

#### Application Example 5

When the same was performed, other than using ethylene glycol along in lieu of using the ethylene glycol mixed solution in Application Example 1, the membrane swelled noticeably. When tensile testing was performed for the membrane, no reduction in strength had occurred at the bent parts. When the membrane was placed in an electrolytic cell and electrolysis performed the same as in Application Example 1, current efficiency was 92%.

#### Application Example 6

When the same was performed, other than using 20 weight percent ethylene glycol and 80 weight percent water, in lieu of using the ethylene glycol mixed solution in Application Example 1, the membrane swelled noticeably. When tensile testing was performed for the membrane, no reduction in strength had occurred at the bent parts. However, when electrolysis was performed with the membrane the same way as in Application Example 1, current efficiency was 93%.

#### Application Example 7

In lieu of using the ethylene glycol mixed solution in Application Example 1, after immersing in ethanol for 20 h at room temperature, [the membrane] was immersed in 2 NNaCL for 20 h at room temperature.

When tensile testing was performed after bending the membrane, no reduction in strength had occurred at the bent parts.

When electrolysis was performed with the membrane the same way as in Application Example 1, current efficiency was 88%. When the membrane was removed after 300 days of electrolysis, hardly any creasing was seen.

#### Application Example 8

A membrane placed horizontally was coated with a bush with the same salt solution, in lieu of immersing in the glycerin mixed salt solution in Application Example 2. When tensile testing was performed after both sides were coated, no reduction in strength had occurred at the bent parts. When the membrane was placed in an electrolytic cell the same way as in Application Example 1, current efficiency was 96%. When the membrane was removed after 300 days of electrolysis, hardly any creasing was seen.